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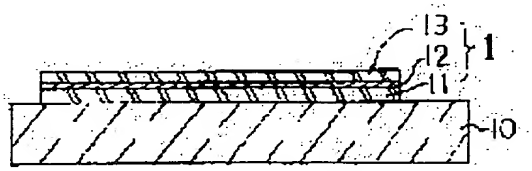
(54) TRANSPARENT CONDUCTIVE FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a transparent conductive thin film high in conductivity and visible light transmittance, without being deteriorated with time and excellent in preservation stability by holding a silver-base thin film between transparent oxide thin films to constitute the three-layer transparent conductive film.
SOLUTION: A silver-base thin film 12 is held between transparent oxide thin films 11 and 13 to constitute a three-layer transparent conductive film 1. The transparent oxide film 13 is the mixed oxide of a first base material contg. ≥1 kind of metallic oxide easy to form a solid soln. with silver and a second base material contg. ≥1 kind of metallic oxide difficult to form a solid soln. with silver, and the silver-base thin film 12 is a silver alloy contg. at least gold.



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審査請求　有　請求項の数６　ＯＬ　（全６頁）　最終頁に続く

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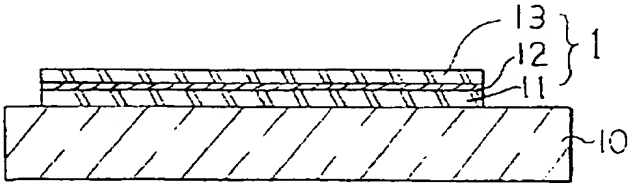
(54)【発明の名称】　透明導電膜

(57)【要約】

【課題】本発明は、銀系薄膜を透明酸化物薄膜で挟持する３層構成の透明導電膜に係わり、特に薄膜で導電性と可視光線透過率が高く、しかも経時劣化がなく保存安定性に優れた透明導電膜を提供することにある。

【解決手段】厚さ５～２０ｎｍの銀系薄膜を透明酸化物薄膜にて挟持する３層構造の透明導電膜において、上記透明酸化物薄膜が、銀と固溶しやすい金属の酸化物を一種以上含む第１の基材と、銀と固溶しにくい金属の酸化物を一種以上含む第２の基材との混合酸化物であり、かつ銀系薄膜が少なくとも金を含有する銀合金であることを特徴とする透明導電膜。



1

【特許請求の範囲】

【請求項１】厚さ５～２０ｎｍの銀系薄膜を透明酸化物薄膜にて挟持する３層構造の透明導電膜において、上記透明酸化物薄膜が、銀と固溶しやすい金属の酸化物を一種以上含む第１の基材と、銀と固溶しにくい金属の酸化物を一種以上含む第２の基材との混合酸化物であり、かつ銀系薄膜が少なくとも金を含有する銀合金であることを特徴とする透明導電膜。

【請求項２】上記銀系薄膜が金を０．１～４at%（原子パーセント）含有する銀合金であることを特徴とする請求項１記載の透明導電膜。

【請求項３】上記銀系薄膜が金を０．１～２．５at%含有する銀合金であることを特徴とする請求項１記載の透明導電膜。

【請求項４】第１の基材が、酸化インジウムであり、第２の基材が、酸化セリウムであることを特徴とする請求項１～３記載の透明導電膜。

【請求項５】透明酸化物薄膜が、酸化セリウムを金属元素換算にて１０～８０at%含有する酸化インジウムとの混合酸化物であることを特徴とする請求項１～４記載の透明導電膜。

【請求項６】透明酸化物薄膜が、酸化セリウムを金属元素換算にて１０～４０at%含有する酸化インジウムとの混合酸化物であることを特徴とする請求項１～５記載の透明導電膜。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、液晶ディスプレイ、入出力装置、あるいはプラズマディスプレイ等の表示装置の透明電極等に用いられる透明導電膜に係り、特に、薄膜で導電性と可視光線透過率が高く、しかも保存安定性に優れた透明導電膜の改良に関するものである。

【０００２】

【従来の技術】ガラス、プラスチックフィルム等の基板上に可視光線を透過する電極形状の透明導電膜が設けられた電極板は、液晶ディスプレイ等の各種表示装置の表示用電極やこの表示装置の表示画面から直接入力する入出力電極等に広く使用されている。

【０００３】この透明導電膜としては、その高い導電性に着目して、酸化インジウム中に酸化錫を添加したＩＴＯ薄膜が広く利用されており、その比抵抗はおよそ２．４×１０$^{-4}$Ω・cmで、透明電極として通常適用される２４０ｎｍの膜厚の場合その面積抵抗はおよそ１０Ω／□である。

【０００４】また、この他にも、酸化錫薄膜、この酸化錫に酸化アンチモンを添加して構成される薄膜（ネサ膜）、酸化亜鉛に酸化アルミニウムを添加して構成される薄膜等が知られているが、これらはいずれも上記ＩＴＯ薄膜よりその導電性が劣り、また、酸やアルカリ等に対する耐薬品性あるいは耐水性等が不十分なため一般には普及していない。

2

【０００５】一方、１９８２年日本で開催された第７回ＩＣＶＭにおいて、熱線反射膜として銀薄膜の表裏面にＩＴＯ薄膜又は酸化インジウム薄膜（ＩＯ薄膜）を積層させて構成される三層構造の透明導電膜が提案されている。この三層構造の透明導電膜はおよそ５Ω／□程度の低い面積抵抗率を有しており、その高い導電性を生かして上記透明電極への応用が期待された。

【０００６】

【発明が解決しようとする課題】ところで、上記ディスプレイ装置や入出力装置においては、近年、画素密度を増大させて緻密な画面を表示することが求められ、これに伴って上記透明電極パターンの緻密化が要求されており、例えば１００μｍ程度のピッチで上記透明電極の端子部を構成することが要求されている。また、液晶ディスプレイ装置において基板に液晶駆動用ＩＣが直接接続される方式（ＣＯＧ）においては、配線の引き回しが幅２０～５０μｍという細線となる部分があり、従来にない高度のエッチング加工適性と高い導電性（低い抵抗率）が要求されている。

【０００７】また、その一方で表示画面の大型化も求められており、このような大画面について上述したような緻密パターンの透明電極を形成し、しかも液晶に充分な駆動電圧を印加できるようにするためには、上記透明電極として５Ω／□以下という高い導電性を備えた透明導電膜を適用する必要があった。また、これに加えて、ＳＴＮ液晶等を利用した単純マトリクス駆動方式の液晶表示装置において１６階調以上の多階調表示を行う場合には３Ω／□以下という更に低い面積抵抗が要求されている。

【０００８】しかしながら、第７回ＩＣＶＭにおいて提案された上記三層構造の透明導電膜においても、高々５Ω／□程度の面積抵抗が得られるに過ぎず、十分な導電性が確保できないという問題点があった。なお、銀薄膜の厚さを１６～１８ｎｍ程度に厚くすることによりその面積抵抗率を約３Ω／□に低下させることは可能であるが、可視光線透過率（特に波長６１０ｎｍ程度の長波長側の可視光線透過率）が７５％程度まで低下し、透明導電膜としての機能が損なわれてしまう。

【０００９】更に、上記三層構造の透明導電膜においては銀の薄膜が積層界面等から侵入した空気中の水分と化合し易く、その表面に酸化物を生成してシミ状の欠陥を生じ、例えば液晶表示装置の透明電極に適用した場合にはその表示画面に表示欠陥等を生じ易いという問題点があった。

【００１０】本発明はこのような問題点に着目してなされたもので、その課題とするところは、薄膜で導電性と可視光線透過率が高く、しかも経時劣化がなく保存安定性に優れた透明導電膜を提供することにある。

【００１１】

【課題を解決するための手段】上述のような技術的課題に鑑みて本発明者等が鋭意検討を重ねたところ、上記三層構造の透明導電膜において、ＩＴＯ薄膜やＩＯ薄膜の代わりに酸化インジウムと酸化セリウム等との混合酸化物から成る透明酸化物を利用すると、その屈折率が増大して光反射率を低下させると共に可視光線透過率を増大させ、導電性に優れた膜厚の厚い銀薄膜を利用ししかも可視光線透過率が高い透明導電膜が得られ、更にこの透明導電膜は極めて高い耐湿性を有することを発見した。本発明はこのような技術的発見に基づいてなされたものである。

【００１２】本発明者らは、５Ω／□以下の低抵抗と高透過率をかねそなえる構成として、０．１～３原子パーセント（以下単にat%という）の銅を含有する銀系薄膜を透明酸化物薄膜で挟持する構造の導電膜も提案しているが、この構成では耐湿性がやや不十分であった。例えば、耐湿性の加速試験として、６０℃、９０%湿度の高温高湿環境下にて１at%銅を含有する銀系薄膜を挟持する構造の導電膜のパターンに微小なシミが発生してしまう欠点があり、不十分であった。

【００１３】すなわち、請求項１に係る発明は、厚さ５～２０ｎｍの銀系薄膜を透明酸化物薄膜にて挟持する３層構造の透明導電膜において、上記透明酸化物薄膜が、銀と固溶しやすい金属の酸化物を一種以上含む第１の基材と、銀と固溶しにくい金属の酸化物を一種以上含む第２の基材との混合酸化物であり、かつ銀系薄膜が少なくとも金を含有する銀合金であることを特徴とする透明導電膜である。

【００１４】この請求項１記載の発明に係る透明導電膜においては、透明酸化物薄膜が、酸化インジウムから成る第１の基材と、酸化チタン、酸化ジルコニウム、酸化ハフニウム、酸化タンタルまたは酸化セリウムから選択された１又は２以上の第２の基材との混合酸化物にて構成されることが、好ましい例である。

【００１５】銀系薄膜において、金を少量含有する銀金合金は、全率固溶（包晶）であり、完全に固溶し合い、銀銅合金（共晶）のように銅の銀合金中での析出がみられないため、可視域でかなり良好な透過率をもっている。銀系薄膜を挟持する構成の導電膜を、ＳＴＮ液晶表示装置のような、５Ω／□以下の低抵抗を要求する単純マトリクス液晶表示装置に用いる場合は、銀合金中の金の添加量を4at%以下に抑えないと５Ω／□以下の低抵抗と、高透過率を両立しにくい。また、逆に銀系薄膜を挟持する構成の導電膜の耐湿性向上への寄与は、０．１at%の少量添加から効果がある。すなわち、請求項２に係る発明は、銀系薄膜が金を０．１～4at%（原子パーセント）含有する銀合金であることを特徴とする。

【００１６】また、エッチング液を用いた透明導電膜のパターニングを前提とする場合、金を２．５at%より多く添加した銀系薄膜を挟持する構成の場合、エッチング後の基板表面に金を中心とする残渣が残りやすいため、さらに好ましくは、金の添加量を２．５at%以下にすることが良い。すなわち、請求項３に係る発明は、銀系薄膜が金を０．１～２．５at%含有する銀合金であることを特徴とする。

【００１７】銀系薄膜を挟持する構成において、酸化インジウムに酸化セリウムを添加していくことは、透明導電膜の耐湿性向上に効果があると同時に、酸化セリウム等の銀と固溶しにくい金属の酸化物の添加量に応じて、透明導電膜の透過率を改善せしめる効果がある。透明導電膜の透過率は、銀系薄膜の膜厚を一定とすると、透明酸化物薄膜の屈折率を高くすることで向上が見込める。本発明者らは、種々の材料を検討した後、低抵抗化と、高透過率、耐湿性およびエッチング加工性の全てを考慮して、透明酸化物薄膜として酸化インジウムと酸化セリウムの混合酸化物を見いだした。すなわち、請求項４に係る発明は、第１の基材が、酸化インジウムであり、第２の基材が、酸化セリウムであることを特徴とする。

【００１８】透明酸化物薄膜として、その屈折率は、２．０～２．４程度の範囲内にあることが望ましい。屈折率は、高い方が良いが、２．４を越えると透明酸化物薄膜そのものからの反射が大きくなり、透明導電膜として高透過率・低反射率を維持しにくくなる。逆に２．０以下の屈折率では、たとえば１５ｎｍの膜厚で挿入された銀系薄膜による光の反射がおさえられなくなり、同様に高透過率・低反射率が保てない。酸化インジウムと酸化セリウムの混合酸化物での酸化セリウムの添加量を金属元素換算にて（酸素元素を除いて換算した）１０～８０at%とすると、その屈折率は、およそ２．０～２．４の範囲となる。すなわち、請求項５に係る発明は、透明酸化物薄膜が、酸化セリウムを金属元素換算にて１０～８０at%含有する酸化インジウムとの混合酸化物であることを特徴とする。

【００１９】単純マトリクス型の液晶表示装置向け透明電極のように、パターン形成を前提とする場合、細かいパターンでのエッチング加工が必要である。本発明において、透明酸化物薄膜中の酸化セリウムを４０at%を越えるレベルとすると、湿式エッチングによるパターン形成がむつかしくなる。望ましくは、酸化セリウムの添加量は、４０at%以下が良い。すなわち、請求項６に係る発明は、透明酸化物薄膜が、酸化セリウムを金属元素換算にて１０～４０at%含有する酸化インジウムとの混合酸化物であることを特徴とする。なお、酸化セリウムと酸化インジウムとの混合酸化物をスパッタリング法にて蒸着する際、原料材料であるスパッターターゲットの密度や導電性、強度を向上させるため、異種の酸化物を少量加えてターゲットとして成形することは可能である。

【００２０】なお、上記銀系薄膜の膜厚が５ｎｍに満たない場合には透明導電膜の導電性が低く、また２０ｎｍを越える場合にはその光透過率が低くなり、いずれの場

合も上記透明導電膜に適さなくなる。

【００２１】また、上記透明酸化物薄膜と銀系薄膜とは、いずれも硝酸をエッチング液としたエッチング処理によりパターニングすることができる。すなわち、基板上に、透明酸化物薄膜、銀系薄膜及び透明酸化物薄膜の三層を成膜して本発明に係る透明導電膜を成膜し、次に表面に露出した透明酸化物薄膜上にレジスト膜をパターン状に形成した後、このレジスト膜から露出した部位を硝酸系エッチング液によってエッチングすることにより、上記三層の薄膜が互いに位置整合したパターン形状にパターニングすることが可能である。このエッチング液としては、硝酸の他、塩酸や硫酸又は酢酸等の他種の酸を硝酸に添加して成る酸等の硝酸系の混酸、あるいは界面活性剤を若干量添加した硝酸が利用できる。

【００２２】また、上記銀系薄膜と透明酸化物薄膜とは、いずれも上述したスパッタリング法によって成膜できる他、真空蒸着法やイオンプレーティング法等の真空成膜法によって成膜することが可能であるが、その生産性の点からスパッタリング法が適している。そして、成膜の際、成膜装置内部の酸素量を制御することにより上記透明酸化物薄膜中の酸素元素含有量を調整してその屈折率をコントロールすることができる。また、この際、銀系薄膜の劣化を防止するため成膜装置内部の水分は少ない方が好ましく、透明酸化物薄膜のエッチング適性を確保するため１８０℃以下又は室温の基板温度で成膜することが望ましい。そして、銀系薄膜と透明酸化物薄膜の全体を１８０℃以下又は室温の基板温度で成膜した後、これら三層膜全体を硝酸系エッチング液でエッチング処理し、次に２００℃以上の温度でアニーリング処理を施すことによりこれら三層膜全体の導電性を増大させることが可能である。

【００２３】次に、本発明に係る透明導電膜を支持する基板としては、例えば、ガラス、プラスチックボード、プラスチックフィルム等が利用できる。また、本発明に係る透明導電膜は、カラーフィルターを備えるかあるいはこれを備えない液晶表示装置の透明電極として適用できる他、ＣＲＴのガラスのフェースプレートを基板としてその表示面に設けてもよい。また、本発明に係る透明導電膜は、太陽電池素子の光入射側に配置される透明電極として利用することも可能である。

【００２４】なお、本発明に係る透明導電膜上に保護層を設けることも可能である。このような保護層としては、例えば、透明合成樹脂やＳｉＯ₂等の透明無機薄膜が適用できる。また、この保護層として低屈折率の樹脂層や光散乱層を適用してＡＲ（反射防止）やＡＧ（アンチ・グレアー）膜として利用することも可能である。

【００２５】ＡＧ膜上に低反射率のＥＭＩ（電磁波シールド）兼用膜として積層することもできる。また、ＡＲの観点から、本発明に係る透明導電膜の上下層、いずれかの部位に屈折率の異なる透明薄膜を積層あるいは挿入して、反射率や透過率の最適化を行なっても良い。

【００２６】請求項１記載の発明に係る透明導電膜によれば、銀系薄膜は銀もしくは銀合金に金を含有するため、銀系薄膜を挟持する構造の導電膜の耐湿性を向上できる。さらに、銅を添加した銀合金による同様構成の導電膜より光透過率の点でより良い導電膜が得られる。請求項２，３記載の発明に係る透明導電膜によれば、金の銀系薄膜への添加量を４ないし 2.5at%以下におさえるため、低抵抗で高透過率の導電膜が、エッチング可能な膜として提供できる。請求項４～６記載の発明に係る透明導電膜によれば、透明酸化物薄膜を高屈折率の透明酸化物薄膜により高透過率・低反射率の導電膜が提供できる。加えて、酸化インジウムへ酸化セリウムを添加することによりエッチング性を保持したまま、耐湿性に富む導電膜が提供できる。

【００２７】

【発明の実施の形態】以下、図面を参照して本発明の実施例について詳細に説明する。

【００２８】

【実施例】

＜実施例１＞この実施例に係る透明導電膜１は、図１に示すように厚さ０．７ｍｍのガラス基板１０上に順次積層された厚さ３３ｎｍの透明酸化物薄膜１１と、厚さ１５ｎｍの銀系薄膜１２、及び、厚さ３４ｎｍの透明酸化物薄膜１３とでその主要部が構成されている。なお、上記透明酸化物薄膜１１，１３は、そのいずれもが酸化セリウムを酸素を除く金属元素換算で３０at%、酸化インジウムの薄膜に加えた混合酸化物とした。また、銀系薄膜１２は、銀に金を１．０at%添加した銀合金である。

【００２９】そして、この透明導電膜１は以下のような方法で成膜されている。まず、ガラス基板１０の表面をアルカリ系界面活性剤と水とで洗浄した後、真空槽内に収容し、逆スパッタリングと呼ばれるプラズマ処理を施してさらに洗浄した。

【００３０】次に、ガラス基板１０を真空槽中から取り出すことなく、このガラス基板１０を室温に維持した状態で、スパッタリング法により透明酸化物薄膜１１、銀薄膜１２及び透明酸化物薄膜１３を順次成膜した。

【００３１】次に、透明酸化物薄膜１３上に電極形状のレジスト膜を形成し、このレジスト膜から露出した部位を硝酸系エッチング液によりエッチングして上記三層の薄膜を互いに位置整合させた状態で電極形状にパターニングし、続いて、２２０℃、１時間のアニール処理を施して上記透明導電膜１を形成した。こうして得られた透明導電膜１の面積抵抗は約２．９Ω／□であった。また、その可視光線透過率を実線にて図２に示す。このパターン形成した透明導電膜１を６０℃、湿度９５%内に５００時間保持した後、表面観察をしたが、何ら外観変化を生じるものではなかった。なお、この混合酸化物による透明導電膜の屈折率を測定したところ２．２４であ

った。

【００３２】＜比較例＞実施例１と同様に、ただし銀系薄膜は銀に銅を１．０at%添加した銀合金とした構成にて、膜厚および製法を同じくして透明導電膜を形成した。可視光線透過率を破線にて図２に併せ示した。実施例１より若干透過率の点で下回った。さらに、比較例の透明導電膜を６０℃、湿度９５%内に保管したところ１９０時間後にシミが発生し不良となった。

【００３３】＜実施例２＞実施例１と同構成、同製法にて、図１に示す透明導電膜１をガラス基板上に形成した。ただし、銀系薄膜１２の膜厚は１５ｎｍと同じであるが、銀系薄膜１２の銀合金の組成を０．１～４at%とした透明導電膜各々の面積抵抗値を表１に示す。なお、面積抵抗値は２２０℃、１時間のアニール処理後に測定した値である。

【００３４】

【表１】

	金の添加量 (at%)							金添加なし
	0.1	0.2	0.4	0.8	1.5	2.5	4.0	(0at%)
面積抵抗値(Ω/□)	2.81	2.83	2.82	2.85	3.28	4.13	4.94	2.81
光透過率(610nm)	93.0	92.8	92.5	92.5	92.4	90.7	89.2	92.6

【００３５】表１に示したように金を４at%添加した銀合金による透明導電膜においても、４．９Ω／□という極めて低い面積抵抗値を有している。２２０℃、１時間のアニール処理後の各々の透明導電膜の光透過率は、５４５ｎｍ（緑色）の波長にていずれも９０%以上であった。６１０ｎｍ（赤色）の波長では、金を４at%添加したもので、８９%と光透過率が少し低下している。光透過率の点からも４at%を越える金の添加は、あまり好ましいものではない。

【００３６】また、各々透明導電膜を６０℃、湿度９５%の高温高湿下に保管し、２００時間後の外観変化を観察したところ、いずれにもシミ発生なく良好であった。また、５００時間同条件で保管した各々の透明導電膜の外観をみたところ、０．４at%以上金を添加したものには外観変化がなかった。０．１at%、０．２at%のものには微小なシミが発生していた。いずれも銅を添加した銀銅合金の比較例より良好であった。なお、金、銅いずれも未添加の純銀による透明導電膜は、６０℃、湿度９５%の高温高湿条件下では２４時間経過後には、大きなシミが発生した。

【００３７】

【発明の効果】本発明の透明導電膜によれば、銀系薄膜を透明酸化物薄膜にて挟持する構造の導電膜であって、銀系薄膜は銀もしくは銀合金に金を含有するため、耐湿性が充分で高光透過率・低抵抗の透明導電膜が提供できることとなった。

【００３８】請求項２，３記載の発明に係る透明導電膜によれば、金の銀系薄膜への添加量を４ないし 2.5%以下におさえるため、低抵抗で高透過率の導電膜が、湿式エッチングにより精緻なパターン形成ができるという利点がある。請求項４～６記載の発明に係る透明導電膜によれば、透明酸化物薄膜を高屈折率・低反射率の導電膜が提供できる。加えて、酸化インジウムへ酸化セリウムを添加することによりエッチング性を保持したまま、耐湿性に富む導電膜が提供できる。

【００３９】

【図面の簡単な説明】

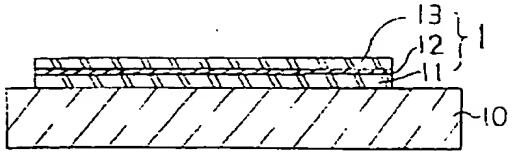
【図１】本発明の透明導電膜の一実施例を示す断面図である。

【図２】本発明の実施例１の透明導電膜の分光透過率と比較例の導電膜の分光透過率を示すグラフ図である。

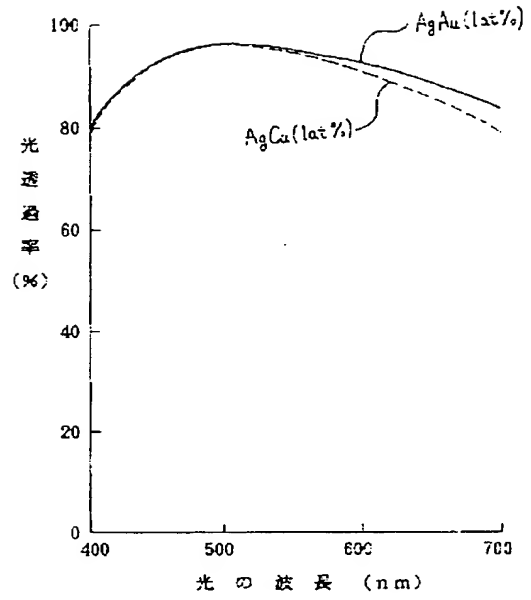
【符号の説明】

１　透明導電膜
１０　ガラス基板
１１　透明酸化物薄膜
１２　銀薄膜
１３　透明酸化物薄膜

【図１】



【図２】



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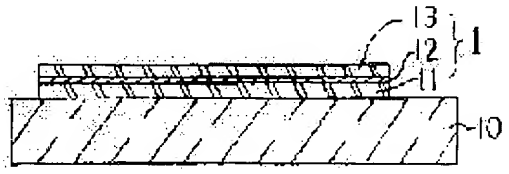
(54) TRANSPARENT CONDUCTIVE FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a transparent conductive thin film high in conductivity and visible light transmittance, without being deteriorated with time and excellent in preservation stability by holding a silver-base thin film between transparent oxide thin films to constitute the three-layer transparent conductive film.
SOLUTION: A silver-base thin film 12 is held between transparent oxide thin films 11 and 13 to constitute a three-layer transparent conductive film 1. The transparent oxide film 13 is the mixed oxide of a first base material contg. ≥1 kind of metallic oxide easy to form a solid soln. with silver and a second base material contg. ≥1 kind of metallic oxide difficult to form a solid soln. with silver, and the silver-base thin film 12 is a silver alloy contg. at least gold.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the transparent electric conduction layer used for the transparent electrode of display, such as a liquid crystal display, an I/O device, or a plasma display, etc., and it is especially related with the enhancement of a transparent electric conduction layer which conductivity and whose visible-ray permeability were high at the thin film, and was moreover excellent in the store stability.
[0002]
[Description of the Prior Art] The electrode plate with which the transparent electric conduction layer of the electrode configuration which penetrates a visible ray was prepared on substrates, such as glass and a plastics film, is widely used for the I/O electrode which carries out a direct input from the display screen of the electrode for a display of various display, such as a liquid crystal display, or this display.
[0003] ITO thin film which added the tin oxide in indium oxide as this transparent electric conduction layer paying attention to the high conductivity is used widely, the specific resistance is 2.4x10-4ohm and cm about, and, in the case of the 240nm thickness usually applied as a transparent electrode, the sheet resistivity is about 10ohm/**.
[0004] Moreover, although the tin-oxide thin film, the thin film (Nesa membrane) constituted by this tin oxide by adding an antimony oxide, the thin film constituted by the zinc oxide by adding an aluminum oxide are known in addition to this, each of these is inferior to the above-mentioned ITO thin film in the conductivity, and since chemical resistance or durability to an acid, alkali, etc. is inadequate, generally they has not spread.
[0005] The transparent electric conduction layer of three layer structures which the front rear face of a silver thin film is made to carry out the laminating of ITO thin film or the indium oxide thin film (IO thin film), and are constituted as a heat ray reflective layer in the 7thICVM held in Japan in 1982 on the other hand is proposed. The transparent electric conduction layer of these three layer structures has the low sheet resistivity about about 5ohms / **, and the application to the above-mentioned transparent electrode was expected taking advantage of the high conductivity.
[0006]
[Problem(s) to be Solved by the Invention] By the way, in the above-mentioned display unit or the I/O device, it is required that it is asked for increasing a pixel density and displaying a precise screen in recent years, and precise-ization of the above-mentioned transparent-electrode pattern is demanded in connection with this, for example, the terminal area of the above-mentioned transparent electrode is constituted from a pitch which is about 100 micrometers. Moreover, in the method (COG) with which the direct file of the IC for a liquid crystal drive is carried out to a substrate in liquid crystal display equipment, there is a fraction from which leading about of a wiring serves as a thin line called the width of face of 20-50 micrometers, and the advanced etching manipulation fitness which is not in the former, and high conductivity (low resistivity) are demanded.
[0007] Moreover, in order to be asked also for large-sized-ization of the display screen on the other hand, to form the transparent electrode of a precise pattern which was mentioned above about such a big screen and to enable it to impress sufficient driver voltage for liquid crystal moreover, the transparent electric conduction layer equipped with the high conductivity of below 5ohms / ** as the above-mentioned transparent electrode needed to be applied. moreover -- in addition, when performing a multi-gradation display of 16 or more gradation in the LCD of a simple matrix drive method using STN LCD etc., the still low sheet resistivity below 3ohms / ** is demanded
[0008] However, also in the transparent electric conduction layer of the three above-mentioned layer structure proposed in the 7thICVM, the sheet resistivity about at most 5ohms / ** did not pass to be obtained, but there was a trouble where sufficient conductivity was not securable. In addition, although it is possible to reduce the sheet resistivity to about 3ohms / ** by making thickness of a silver thin film thick about 16-18nm, visible-ray permeability (especially a long wave with a wavelength of about 610nm visible-ray permeability by the side of merit) falls to about 75%, and the function as a transparent electric conduction layer will be spoiled.
[0009] Furthermore, when it was easy to combine with the moisture in the air into which the silver thin film invaded from the laminating interface etc. in the transparent electric conduction layer of the three above-mentioned layer structure, and an oxide was generated on the front face, and a silverfish-like defect was produced, for example, it applied to the transparent electrode of a LCD, the trouble of being easy to produce a display defect etc. was shown in the display screen.
[0010] It is in offering the transparent electric conduction layer which this invention was made paying attention to such a trouble, and conductivity and whose visible-ray permeability are [the place made into the technical probrem] high at a thin film, moreover does not have a degradation with the passage of time, and was excellent in the store stability.
[0011]
[Means for Solving the Problem] When this invention person etc. repeats a study zealously in view of the above technical technical probrems, it sets on the transparent electric conduction layer of the three above-mentioned layer structure. If the

transparent oxide which consists of mixed oxides, such as indium oxide and a cerium oxide, instead of ITO thin film or IO thin film is used The refractive index increases, while the rate of a light reflex is reduced, visible-ray permeability is increased, the thick silver thin film of the thickness excellent in conductivity is used, moreover the transparent electric conduction layer with high visible-ray permeability is obtained, and this transparent electric conduction layer discovered having very high moisture resistance further. this invention is made based on such technical discovery.

[0012] Although this invention persons had also proposed the electric conduction layer of the structure which pinches the silver system thin film which serves both as and offers the low resistance below 5ohms / **, and high permeability, and which contains the copper of 0.1 - 3 atomic ratio (only henceforth at%) as a configuration by the transparent oxide thin film, this configuration was [moisture resistance] a little insufficient. For example, as a damp-proof accelerated test, the fault which a minute silverfish generates was in the pattern of the electric conduction layer of the structure which pinches the silver system thin film containing 1at% copper, and its bottom of 60 degrees C, and 90% high-humidity/temperature environment of humidity was inadequate for it.

[0013] Namely, invention concerning a claim 1 sets a silver system thin film with a thickness of 5-20nm on the transparent electric conduction layer of a three-tiered structure pinched in a transparent oxide thin film. It is the transparent electric conduction layer characterized by being the mixed oxide of the 1st base material in which the above-mentioned transparent oxide thin film contains the oxide of the metal which is easy to dissolve with silver more than a kind, and the 2nd base material which contains the oxide of the metal which seldom dissolves with silver more than a kind, and being the silver alloy in which a silver system thin film contains gold at least.

[0014] In the transparent electric conduction layer concerning this invention according to claim 1, it is a desirable example to consist of a mixed oxide with the 2nd 1 or 2 or more base material as which the transparent oxide thin film was chosen from the 1st base material which consists of indium oxide, titanium oxide and a zirconium oxide, an oxidization hafnium, tantalum oxide, or the cerium oxide.

[0015] In the silver system thin film, the silver gold alloys which carry out little inclusion of the gold are all rate dissolution (peritectic), and since it dissolves each other completely and a precipitation in a copper silver alloy is not seen like a silver copper alloy (eutectic), they have quite good permeability by the visible region. When using the electric conduction layer of a configuration of pinching a silver system thin film for the simple matrix LCD which demands low resistance below 5ohms / ** like STN LCD, if the addition of the gold in a silver alloy is not held down to less than [4at%], it is hard to be compatible with the low resistance below 5ohms / ** in high permeability. Moreover, contribution of a up to [the moisture-proof disposition of the electric conduction layer of a configuration of pinching a silver system thin film conversely] is effective from 0.1at% of little addition. namely, invention concerning a claim 2 -- a silver system thin film -- gold -- 0.1 - 4at% (atomic ratio) -- it is characterized by being the silver alloy to contain

[0016] Moreover, when premised on patterning of the transparent electric conduction layer using the etching reagent, in order that the residue centering on gold may tend to remain in the substrate front face after etching in a configuration of pinching the silver system thin film which added more gold than 2.5at%, it is good to make a golden addition into less than [2.5at%] still preferably. namely, invention concerning a claim 3 -- a silver system thin film -- gold -- 0.1 - 2.5at% -- it is characterized by being the silver alloy to contain

[0017] In the configuration which pinches a silver system thin film, it is effective in making the permeability of a transparent electric conduction layer improve to add a cerium oxide to indium oxide according to the addition of the oxide of the metal which seldom dissolves with silver, such as a cerium oxide, while an effect is on the moisture-proof disposition of a transparent electric conduction layer. If the permeability of a transparent electric conduction layer sets the thickness of a silver system thin film constant, enhancement can be expected by making high the refractive index of a transparent oxide thin film. This invention persons found out the mixed oxide of indium oxide and a cerium oxide as a transparent oxide thin film in consideration of all of the reduction in resistance, high permeability and moisture resistance, and etching workability, after examining various materials. That is, the 1st base material is indium oxide and invention concerning a claim 4 is characterized by the 2nd base material being a cerium oxide.

[0018] As for the refractive index, as a transparent oxide thin film, it is desirable that it is within the limits of 2.0 to about 2.4. Although the higher one of a refractive index is good, if 2.4 is exceeded, the reflex from the transparent oxide thin film itself will become large, and it will seldom come to maintain high permeability and a low reflection factor as a transparent electric conduction layer. Conversely, in 2.0 or less refractive index, it stops pressing down reflex of the light by the silver system thin film inserted, for example by the 15nm thickness, and high permeability and a low reflection factor cannot be kept the same. If the addition of the cerium oxide in the mixed oxide of indium oxide and a cerium oxide is made into 10 (it converted except for oxygen element), - 80at% by metallic element conversion, the refractive index will serve as about 2.0 to 2.4 domain. namely, invention concerning a claim 5 -- a transparent oxide thin film -- a cerium oxide -- a metallic element conversion -- 10 - 80at% -- it is characterized by being a mixed oxide with the indium oxide to contain

[0019] Like the simple matrix type transparent electrode for LCDs, when premised on pattern formation, the etching manipulation with a fine pattern is required. In this invention, if the cerium oxide in a transparent oxide thin film is made into the level exceeding 40at%, the pattern formation by wet etching will become difficult. Desirably, as for the addition of a cerium oxide, less than [40at%] is good. namely, invention concerning a claim 6 -- a transparent oxide thin film -- a cerium oxide -- a metallic element conversion -- 10 - 40at% -- it is characterized by being a mixed oxide with the indium oxide to contain In addition, since the density of the spatter target which is a raw material material, and conductivity and an intensity are raised in case the vacuum evaporationo of the mixed oxide of a cerium oxide and indium oxide is carried out by the sputtering method, it is possible to fabricate an oxide of a different kind as small quantity, in addition a target.

[0020] In addition, when the thickness of the above-mentioned silver system thin film does not fulfill 5nm, the conductivity of a transparent electric conduction layer is low, and in exceeding 20nm, the light transmittance becomes low and neither of the cases stops being suitable for the above-mentioned transparent electric conduction layer.

[0021] Moreover, patterning of each of above-mentioned transparent oxide thin films and silver system thin films can be carried

out by etching processing which made the nitric acid the etching reagent. Namely, the transparent electric conduction layer which forms three layers, a transparent oxide thin film, a silver system thin film, and a transparent oxide thin film, and is applied to this invention on a substrate is formed. Next, after forming a resist layer in the shape of a pattern on the transparent oxide thin film exposed to the front face, it is possible to carry out patterning of the site exposed from this resist layer to the pattern configuration in which the thin film of the three above-mentioned layers carried out position matching mutually by etching by the nitric-acid system etching reagent. The mixed acid of nitric-acid systems, such as an acid which adds the acid of other types, such as others, a hydrochloric acid, and a sulfuric acid or an acetic acid, to a nitric acid, and changes as this etching reagent, or the nitric acid which carried out amount addition of the surfactant a little can be used. [nitric acid]

[0022] Moreover, although each of above-mentioned silver system thin films and transparent oxide thin films can be formed by the sputtering method mentioned above, and also they can form membranes by the vacuum forming [membranes] methods, such as a vacuum deposition method and the ion-plating method, the sputtering method is suitable from the point of the productivity. And in the case of membrane formation, by controlling the amount of oxygen inside membrane formation equipment, the oxygen element content in the above-mentioned transparent oxide thin film can be adjusted, and the refractive index can be controlled. Moreover, in this case, in order to prevent a degradation of a silver system thin film, the moisture inside membrane formation equipment has the fewer desirable one, and in order to secure the etching fitness of a transparent oxide thin film, it is desirable to form membranes at 180 degrees C or less or the substrate temperature of a room temperature. And after forming a silver system thin film and the whole transparent oxide thin film at 180 degrees C or less or the substrate temperature of a room temperature, it is possible to increase the conductivity of these whole 3 layer membrane by carrying out etching processing of these whole 3 layer membrane by the nitric-acid system etching reagent, and next performing annealing processing at the temperature of 200 degrees C or more.

[0023] Next, as a substrate which supports the transparent electric conduction layer concerning this invention, glass, a plastics board, a plastics film, etc. can be used, for example. Moreover, the transparent electric conduction layer concerning this invention is applicable as a transparent electrode of the LCD which is equipped with a light filter or is not equipped with this, and also may use the face plate of the glass of CRT as a substrate, and may prepare it in the screen. Moreover, the transparent electric conduction layer concerning this invention can also be used as a transparent electrode arranged at the optical incidence side of a solar battery element.

[0024] In addition, it is also possible to prepare a protection layer on the transparent electric conduction layer concerning this invention. As such a protection layer, it is a lucite and SiO2, for example. The transparent inorganic thin film of a grade is applicable. Moreover, it is also possible to use as AR (acid resisting) or an AG (anti-********) layer as this protection layer with the application of the resin layer and light-scattering layer of a low refractive index.

[0025] A laminating can also be carried out as an EMI (electromagnetic wave shield) combination layer of a low reflection factor on AG layer. moreover, the transparent thin film from which a refractive index is different from the viewpoint of AR to the site of the vertical layer [either] of the transparent electric conduction layer concerning this invention -- a laminating -- or it may insert and an optimization of a reflection factor or permeability may be performed

[0026] According to the transparent electric conduction layer concerning invention according to claim 1, since a silver system thin film contains gold in silver or a silver alloy, it can improve the moisture resistance of the electric conduction layer of the structure which pinches a silver system thin film. furthermore, it is based on the silver alloy which added copper -- the electric conduction layer better than the electric conduction layer of a configuration in respect of a light transmittance is obtained similarly ** [according to a claim 2 and the transparent electric conduction layer concerning invention of three publications, there is no 4 about the addition to a golden silver system thin film] Since it presses down less than [2.5at%], the electric conduction layer of high permeability in low resistance can provide as a layer which can etch. According to the transparent electric conduction layer concerning invention according to claim 4 to 6, the electric conduction layer of high permeability and a low reflection factor can offer a transparent oxide thin film by the transparent oxide thin film of a high refractive index. In addition, the electric conduction layer which is rich in moisture resistance can be offered, holding etching nature by adding a cerium oxide to indium oxide.

[0027]

[Embodiments of the Invention] Hereafter, with reference to a drawing, the example of this invention is explained in detail.

[0028]

[Example]

<Example 1> The principal part consists of a transparent oxide thin film 11 with a thickness [by which the laminating was carried out one,by one on the glass substrate 10 with a thickness of 0.7mm as the transparent electric conduction layer 1 concerning this example was shown in drawing 1] of 33nm, and the silver system thin film 12 with a thickness of 15nm and the transparent oxide thin film 13 with a thickness of 34nm. in addition, the above-mentioned transparent oxide thin films 11 and 13 -- the any -- although -- the cerium oxide was made into the mixed oxide added to the thin film of indium oxide 30at% by the metallic element conversion except oxygen moreover, the silver system thin film 12 -- silver -- gold -- 1.0at% -- it is the added silver alloy

[0029] And this transparent electric conduction layer 1 is formed by the following technique. First, after an alkali system surfactant and water washed the front face of a glass substrate 10, it held in the vacuum tub, the plasma treatment called reverse sputtering was given, and it washed further.

[0030] Next, without taking out a glass substrate 10 out of a vacuum tub, where this glass substrate 10 is maintained to a room temperature, the transparent oxide thin film 11, the silver thin film 12, and the transparent oxide thin film 13 were formed one by one by the sputtering method.

[0031] Next, the resist layer of an electrode configuration was formed on the transparent oxide thin film 13, where it etched the site exposed from this resist layer by the nitric-acid system etching reagent and position matching of the thin film of the three above-mentioned layers is carried out mutually, patterning was carried out to the electrode configuration, then annealing processing of 220 degrees C and 1 hour was performed, and the above-mentioned transparent electric conduction layer 1 was

formed. In this way, the sheet resistivity of the obtained transparent electric conduction layer 1 was about 2.9ohm/**. Moreover, the visible-ray permeability is shown in drawing 2 as a solid line. Although surface observation was carried out after holding this transparent electric conduction layer 1 that carried out pattern formation in 60 degrees C and 95% of humidity for 500 hours, it was not what produces appearance change at all. In addition, it was 2.24 when the refractive index of the transparent electric conduction layer by this mixed oxide was measured.

[0032] the <example of comparison> example 1 -- the same -- however, a silver system thin film -- silver -- copper -- 1.0at% -- with the configuration made into the added silver alloy, the thickness and the process were made the same and the transparent electric conduction layer was formed Visible-ray permeability was combined and shown in drawing 2 with the dashed line. It was less in respect of permeability a little from the example 1. Furthermore, when the transparent electric conduction layer of the example of a comparison was saved in 60 degrees C and 95% of humidity, 190 hours after, the silverfish occurred and it became poor.

[0033] The transparent electric conduction layer 1 shown in drawing 1 by the <example 2> example 1, and this configuration and this process was formed on the glass substrate. however, although the thickness of the silver system thin film 12 is the same as that of 15nm, the sheet resistivity value of each transparent electric conduction layer which made composition of the silver alloy of the silver system thin film 12 0.1 - 4at% is shown in Table 1 In addition, a sheet resistivity value is a value measured after annealing processing of 220 degrees C and 1 hour.

[0034]

[Table 1]

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[0035] it was shown in Table 1 -- as -- gold -- 4at% -- also in the transparent electric conduction layer by the added silver alloy, it has the very low sheet resistivity value of 4.9ohm/** All were 90% or more on the wavelength whose light transmittance of each transparent electric conduction layer after annealing processing of 220 degrees C and 1 hour is 545nm (green). the wavelength of 610nm (red) -- gold -- 4at% -- it is what was added and 89% and the light transmittance are falling for a while Addition of the gold which exceeds 4at% also from the point of a light transmittance is not not much desirable.

[0036] Moreover, it was [that there is no silverfish occurrence in all] good, when the transparent electric conduction layer was respectively saved under 60 degrees C and the high-humidity/temperature of 95% of humidity and appearance change 200 hours after was observed. Moreover, when the appearance of each transparent electric conduction layer saved on these conditions for 500 hours was seen, there was no appearance change in what added more than 0.4at% gold. 0. In the 0.2at% thing, the minute silverfish had occurred 1at%. All were better than the example of a comparison of the silver copper alloy which added copper. in addition, gold and copper -- in all, under 60 degrees C and the high-humidity/temperature condition of 95% of humidity, the big silverfish generated the transparent electric conduction layer by non-added virgin silver after 24 hour progress

[0037]

[Effect of the Invention] According to the transparent electric conduction layer of this invention, it is the electric conduction layer of the structure,which pinches a silver system thin film in a transparent oxide thin film, and since a silver system thin film contains gold in silver or a silver alloy, its moisture resistance will be enough and it can offer the transparent electric conduction layer of a high light transmittance and low resistance.

[0038] ** [according to a claim 2 and the transparent electric conduction layer concerning invention of three publications, there is no 4 about the addition to a golden silver system thin film] In order to press down to 2.5% or less, there is an advantage that minute pattern formation can do the electric conduction layer of high permeability in low resistance by wet etching. According to the transparent electric conduction layer concerning invention according to claim 4 to 6, the electric conduction layer of a high refractive index and a low reflection factor can offer a transparent oxide thin film. In addition, the electric conduction layer which is rich in moisture resistance can be offered, holding etching nature by adding a cerium oxide to indium oxide.

[0039]

[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] The transparent electric conduction layer characterized by being the mixed oxide of the 1st base material in which the above-mentioned transparent oxide thin film contains the oxide of the metal which is easy to dissolve with silver more than a kind in the transparent electric conduction layer of the three-tiered structure which pinches a silver system thin film with a thickness of 5-20nm in a transparent oxide thin film, and the 2nd base material which contains the oxide of the metal which seldom dissolves with silver more than a kind, and being the silver alloy in which a silver system thin film contains gold at least.
[Claim 2] the above-mentioned silver system thin film -- gold -- 0.1 - 4at% (atomic ratio) -- the transparent electric conduction layer according to claim 1 characterized by being the silver alloy to contain
[Claim 3] the above-mentioned silver system thin film -- gold -- 0.1 - 2.5at% -- the transparent electric conduction layer according to claim 1 characterized by being the silver alloy to contain
[Claim 4] The transparent electric conduction layer according to claim 1 to 3 characterized by for the 1st base material being indium oxide and the 2nd base material being a cerium oxide.
[Claim 5] a transparent oxide thin film -- a cerium oxide -- a metallic element conversion -- 10 - 80at% -- the transparent electric conduction layer according to claim 1 to 4 characterized by being a mixed oxide with the indium oxide to contain
[Claim 6] a transparent oxide thin film -- a cerium oxide -- a metallic element conversion -- 10 - 40at% -- the transparent electric conduction layer according to claim 1 to 5 characterized by being a mixed oxide with the indium oxide to contain

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the cross section showing one example of the transparent electric conduction layer of this invention.
[Drawing 2] It is the graphical representation showing the spectral transmittance of the transparent electric conduction layer of the example 1 of this invention, and the spectral transmittance of the electric conduction layer of the example of a comparison.
[Description of Notations]
1 Transparent Electric Conduction Layer
10 Glass Substrate
11 Transparent Oxide Thin Film
12 Silver Thin Film
13 Transparent Oxide Thin Film

[Translation done.]